

AD-A043 532

CHICAGO UNIV ILL

CO₂ PRODUCT VELOCITY DISTRIBUTION FOR CO OXIDATION ON PLATINUM. (U)

JUL 77 C A BECKER, J P COWIN, L WHARTON

N00014-77-C-0240

F/G 7/4

NL

UNCLASSIFIED

| OF |

AD
A043532



END
DATE
FILMED

9 -77

DDC

AD A 043532

6 CO_2 PRODUCT VELOCITY DISTRIBUTIONS FOR
CO OXIDATION ON PLATINUM

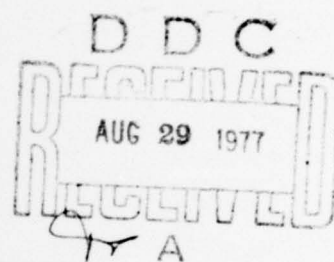
10 Charles A. Becker, James P. Cowin and Lennard Wharton
The James Franck Institute
and the Department of Chemistry
The University of Chicago
Chicago, Illinois 60637

and

Daniel J. Auerbach

Department of Chemistry
Johns Hopkins University
Baltimore, Maryland 21218

Journal
article
Daniel J.
Auerbach



11 Jul 77

12 9p.

15 N00014-77-C-0240, AF-AFOSR-3186-77

It has been inferred^{1,2} from the very peaked ($\cos^2 \theta$) angular distribution of the CO_2 formed by catalytic oxidation of CO on Pt (111) that the product CO_2 is desorbed with excess translational kinetic energy. We report here the first direct measurement of the CO_2 velocity distributions and angular distributions for this reaction on polycrystalline Pt. These quantitatively confirm the inference: For example the most probable CO_2 energy is 3560° K, perpendicular from Pt at 880° K.

The experiment was performed in an ultra-high vacuum system equipped with a rotatable doubly differentially pumped mass spectrometer detector and a quadruply pumped molecular beam source. Further details of the apparatus have been given elsewhere.³ A collimated (1° FWHM) supersonic molecular beam with kinetic energy $E/k = 980$ K mechanically chopped into pulses of approximately 21 microseconds FWHM

AU NO.
DDC FILE COPY

082 450

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

hit a polycrystalline Pt foil. The Pt was maintained at temperatures between 300° K and 1100° K in oxygen atmospheres of 5×10^{-8} to 5×10^{-6} torr. The peak CO pulse intensity was approximately $10^{15} / \text{cm}^2 / \text{sec}$ at the surface, with a duty factor of 1%. The surface had been cleaned by standard techniques.⁴ Auger electron spectroscopy of the cleaned Pt indicated only oxygen and calcium (5 - 10%) as surface contaminants. Because the system was pumped with a very small, 11ℓ/sec, ion pump when oxygen was applied, the surface oxygen was not substantially depleted due to reaction with ambient CO.⁵ Ion pump conversion of O_2 to CO produced a CO/O_2 ratio of less than 1/1000 in the chamber.

Fig. 1 shows distributions of the time elapsed from the point at which the CO pulse reaches the sample position to the time the indicated species is ionized (14.45 cm away). 1 (a) characterizes the CO beam when allowed directly into the detector. 1 (b) and (c) characterize the residence plus flight time of CO_2 product emitted at angles of 0° and 45° (specular) from the surface normal, with a surface temperature $T_s = 880^\circ \text{ K}$ and an average O_2 pressure of 1×10^{-7} torr. As discussed further below, there is a regime of surface temperatures and O_2 pressures for which residence time is negligible compared to flight time. The data shown in figure 1 were obtained under such conditions and thus directly give velocity distributions. Any disregarded residence time would only increase the inferred CO_2 velocity. For CO_2 desorbing in the normal direction the most probable velocity was $1.16 \times 10^5 \text{ cm/sec}$, implying a kinetic energy of $E/k = 3560^\circ \text{ K}$. At larger

White Section	<input checked="" type="checkbox"/>
Ball Section	<input type="checkbox"/>
	<input type="checkbox"/>
8*	
CONTRIBUTION AVAILABILITY CODES	
INT.	AVAIL. AND/OR SPECIAL
A	

angles from the surface normal the most probable velocity decreases monotonically. At 45° it is 9×10^4 cm/sec for a kinetic energy of $E/k = 2140^\circ$. When transformed to number density velocity distributions the data show speed ratios (FWHM/most probable velocity) of $.88 \pm .12$ and $1.11 \pm .23$ for the desorption at 0° and 45° from the normal respectively. The speed ratio for a thermal distribution is 1.155. Both results are qualitatively similar to the results of Comsa et al for H_2 desorption from a sulfur contaminated nickel surface.⁶

As surface temperatures are lowered progressively from 650 to 425 K the elapsed time distributions become increasingly broader with a tail to long times. For example, for O_2 pressure of 3×10^{-7} torr, Pt at 428 K, the decay time of the tail is 464 μ sec. As the temperature is raised above approximately 650° K the width of distributions is essentially independent of temperature (and the peak shifts progressively to shorter times). The results below 650° K show decay times thought to be characteristic of surface diffusion of reactants.⁵ Further evidence for this effect was that higher ambient O_2 pressures gave sharper distributions in the lower temperature regime. This diffusion limited behavior is characteristic of the Langmuir-Hinshelwood reaction mechanism.

The present velocity distributions are remarkably narrow for a polycrystalline sample. The decrease of velocity with angle from normal is inconsistent with a unique 1-dimensional barrier model such as proposed by van Willigen⁷ which gives the opposite trend. Nevertheless it is possible that a diversity of reaction sites and hence barriers could produce the observed trend: High barrier high velocity products would be concentrated at small angles and low barrier low velocity

products would be spread to wider angles where they would be preferentially observed. Clarification of the applicability of a barrier model awaits further experiments with single crystal samples.

Previous molecular beam studies of this reaction had shown sharply peaked number density angular distributions. Palmer and Smith¹ reported $\cos^d \theta$ with d ranging from 4 to 6, for various (111) samples studied. Employing a barrier model,⁷ Palmer² interpreted these results as implying a barrier to adsorption for CO_2 of 7 kcal/mole (3500° K). This result is comparable to our finding a peak kinetic energy of 3650° K for desorption in the normal direction (at $T_s = 880^\circ\text{K}$). For our polycrystalline sample we find d values of 2 to 3. The discrepancy in d cannot be attributed simply to the distribution of surface normals for the various exposed faces. Helium scattering from this sample showed a FWHM of 18° implying a FWHM distribution of surface normal directions of 9° , and convoluting this distribution with a $\cos^6 \theta$ distribution reduces the exponent d to only 5.75.

Acknowledgment

This research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-77-3186, and by the Office of Naval Research, Contract No. N00014-77-0240.

References

1. R. L. Palmer and J. N. Smith, Jr., J. Chem. Phys. 60, 1453 (1974).
2. R. L. Palmer and J. N. Smith, Catalysis Reviews - Science and Engineering 12, 279 (1976) and R. L. Palmer, Private Communication.
3. D. J. Auerbach, C. A. Becker, J. P. Cowin and L. Wharton, Appl. Phys. (in press).
4. A. E. Morgan and G. A. Somorjai, Surface Sci. 12, 405 (1968).
5. H. Hopster, H. Ibach and G. Comsa, J. Catal, 46, 37 (1977).
6. G. Comsa, R. David, K. D. Rendulic, "VI International Symposium on Molecular Beams" (FOM -Institute, Amsterdam 1977) Vol. II, P. 221.
7. W. Van Willigen, Phys. Lett. A, 28, 80 (1968).

Figure Caption

Fig. 1) Elapsed time distributions (and with subtraction of background) at ambient Oxygen Pressure = 1×10^{-7} torr, $T = 880^\circ \text{ K}$: a.) CO beam, b.) CO_2 product at 0° from normal, c.) CO_2 product at 45° from normal. Flight path = 14.45 cm.

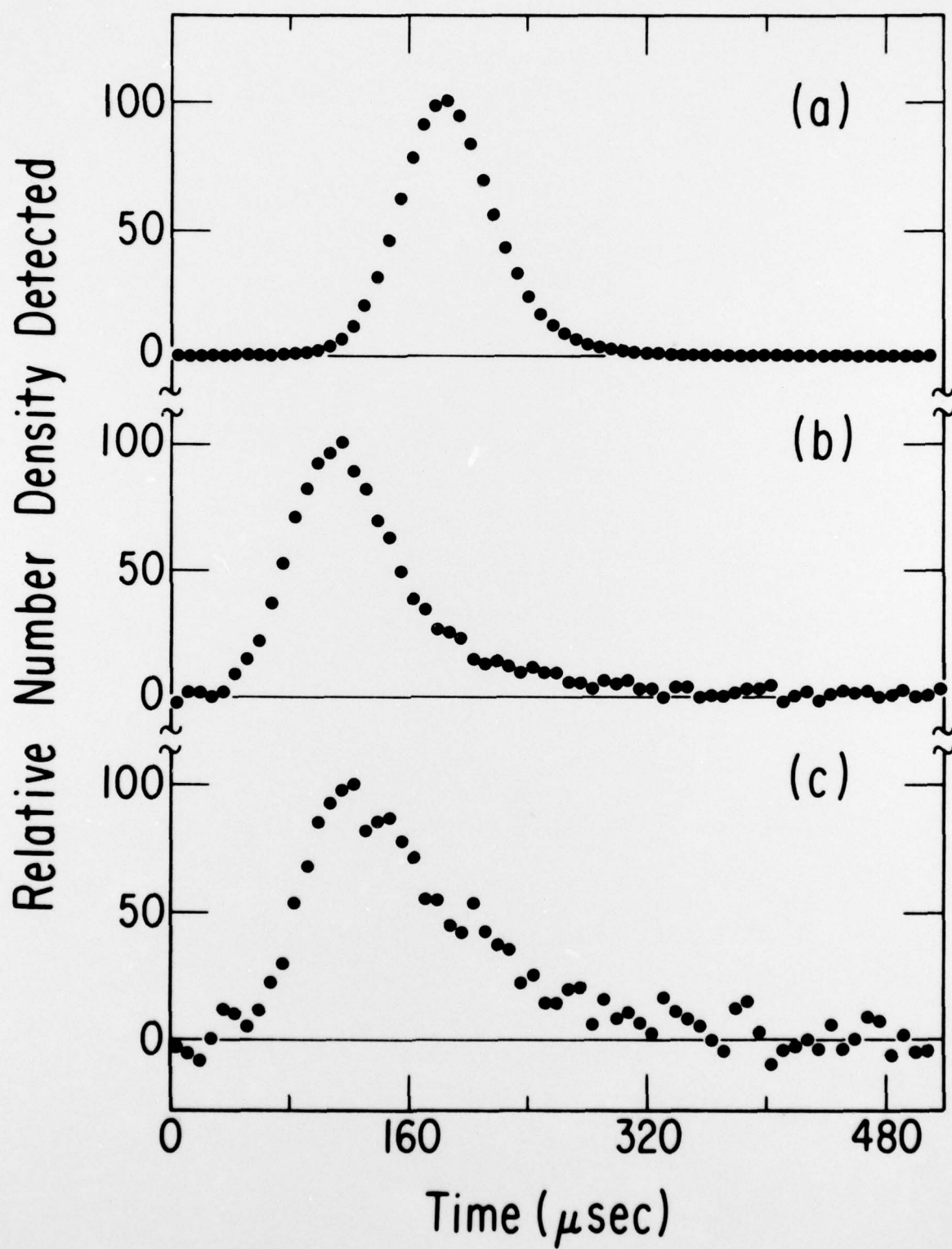


Fig.1

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CO ₂ PRODUCT VELOCITY DISTRIBUTIONS FOR CO OXIDATION ON PLATINUM		5. TYPE OF REPORT & PERIOD COVERED Journal Article
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Charles A. Becker, James P. Cowin and Lennard Wharton University of Chicago and Daniel J. Auerbach, Johns Hopkins University		8. CONTRACT OR GRANT NUMBER(s) ONR # N00014-77-C-0240 AF-AEDSR-3180-77
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lennard Wharton, James Franck Inst. and Dept. Chem. University of Chicago, 5640 S. Ellis Ave. Chicago, IL 60637		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Physics Program Office Arlington, VA 22217		12. REPORT DATE July, 1977
		13. NUMBER OF PAGES 7
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES To be published in J. Chem. Phys.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Platinum catalyst Oxidation CO oxidation Velocity Distribution		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) It has been inferred from the very peaked ($\cos^2 \theta$) angular distribution of the CO ₂ formed by catalytic oxidation of CO on Pt (111) that the product CO ₂ is desorbed with excess translational kinetic energy. We report here the first direct measurement of the CO ₂ velocity distributions and angular distributions for this reaction on polycrystalline Pt. These qualitatively confirm the inference and give quantitative information. For CO ₂ desorbing in the normal direction the most probable velocity was 1.16×10^5 cm/sec, implying a kinetic energy of $E/k = 3560^\circ \text{K}$. At larger angles from the surface normal		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

116000

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. Abstract (cont'd.)

the most probable velocity decreases monotonically. At 45° it is 9×10^4 cm/sec for a kinetic energy of $E/k = 2140^\circ$ degrees.

degrees

90000

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)